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(54) Title of the Invention : Inorganic Antimicrobial Agent whose Surface is Coated with Polyurethane Resin, Process for the Production thereof and Antimicrobial Resin Composition

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Specification

1. Title of the Invention : Inorganic Antimicrobial Agent whose Surface is Coated with Polyurethane Resin, Process for the Production thereof and Antimicrobial Resin Composition

2. What we claim is:

1. An antimicrobial agent characterized in that the surface of at least one kind of inorganic antimicrobial agent particles that are capable of eluting silver and / or copper metal ions, is coated with a polyurethane resin.
2. A process for the production of an antimicrobial agent characterized in that at least one kind of inorganic antimicrobial agent particles that are capable of eluting silver and / or copper metal ions, at least one kind of poly isocyanate compounds and / or at least one kind of compounds having 2 or more active hydrogen - containing groups are mixed, and the surface of the above - mentioned inorganic antimicrobial agent particles is

coated with a polyurethane resin.

3. An antimicrobial resin composition containing an inorganic antimicrobial agent coated with a polyurethane resin, in accordance with Claim 1.

3. Detailed Explanation of the Invention

[Utilization Fields in the Industry]

The present invention relates to an inorganic antimicrobial agent whose surface is coated with a polyurethane resin, said inorganic antimicrobial agent being capable of providing an antimicrobial resin composition that can be dispersed well in a resin, and is excellent in heat resistance and light resistance.

[Conventional Technology]

An inorganic antimicrobial agent obtained by first coating an inorganic antimicrobial agent particles with a discoloring prevention agent for resin, and then being coated with a wax, can provide an excellent antimicrobial resin composition excellent in dispersibility without heat and light

discoloration, when kneaded with a resin. However, as the films of a discoloration prevention agent for resin and a wax that coat the surface of an antimicrobial agent are inferior in heat resistance and strength, if a processing temperature is high and depending on a type of a resin, discoloration due to heat or light could not be completely or perfectly prevented. Especially for use that requires transparency, they could not be utilized.

In addition, antimicrobial resin compositions in which an inorganic antimicrobial agent is blended in a resin have been known in the art (Japanese Patent Gazette, Patent Publication No. Sho 63 / 1988 – 54013, Japanese Laid Open Patent Gazette, Laid Open Patent Publication No. Sho 63 / 1988 – 265958, Japanese Laid Open Patent Gazette, Laid Open Patent Publication No. Hei 1 / 1989 – 167212 and Japanese Laid Open Patent Gazette, Laid Open Patent Publication No. Hei 1 / 1989 – 213410). With these arts, it is stated that an antimicrobial property can be imparted simply by blending inorganic antimicrobial agent particles in a resin by a conventional process. However, since the surface of inorganic

antimicrobial agent particles is hydrophilic, poor dispersion may result when they are kneaded in a hydrophobic resin. In addition, there has been a large problem in that as the surface of the inorganic antimicrobial agent particles has been activated, and the silver and copper ions present there are extremely high in reactivity, they react with a resin and additives and a residue of a catalyst, etc. contained therein, causing discoloration in resin, and thus the commercial value thereof is markedly damaged.

[Problem Points which the Present Invention Tries to Solve]

The present invention has been achieved to overcome such defects of conventional inorganic antimicrobial agents and to provide an inorganic antimicrobial agent that is good in dispersion in resin and does not discolor a resin.

[Means by which to Solve the Problem Points]

The present invention is to provide an inorganic antimicrobial agent with an excellent antimicrobial property without discoloring a resin at all, by coating the surface of inorganic antimicrobial agent particles with a polyurethane resin, thereby improving the affinity to a resin, a process for

the production thereof and an antimicrobial resin composition.

In the following, we shall explain the present invention.

As inorganic antimicrobial agents capable of eluting metal ions of silver and / or copper to be used in the present invention, mention may be made of antimicrobial zeolite, an antimicrobial alumino silicate, an antimicrobial intercalation compound, antimicrobial soluble glass, a silver salt compound, a copper salt compound, etc., however it is to be understood that they are not limited only to the above - mentioned ones.

As antimicrobial zeolite, for example, use can be made of, without any restriction, zeolite obtained by replacing with ions capable of eluting silver and / or copper ions, ion – exchangeable ions in zeolite disclosed in Japanese Patent Gazette, Patent Publication No. Sho 63 / 1988 – 54013, Japanese Laid Open Patent Gazette, Laid Open Patent Publication No. Sho 60 / 1985 – 1810022, Japanese Laid Open Patent Gazette, Laid Open Patent Publication No. Sho 63 / 1988 – 265809, Japanese Laid Open Patent Gazette, Laid Open Patent Publication No. Hei 2 / 1990 – 111709, etc.

As an antimicrobial alumino silicate, for example, use can be made of, without any restriction, zeolite obtained by replacing with ions capable of eluting silver and / or copper ions, ion – exchangeable ions in zeolite disclosed in Japanese Laid Open Patent Gazette, Laid Open Patent Publication No. Sho 62 / 1987 – 70221, Japanese Laid Open Patent Gazette, Laid Open Patent Publication No. Hei 1 / 1989 – 167212, etc.

As an antimicrobial intercalation compound, for example, use can be made of, without any restriction, an intercalation compound capable of eluting silver and / or copper ions in which a silver complex salt is carried between layers of an inorganic intercalation compound disclosed in Japanese Laid Open Patent Gazette, Laid Open Patent Publication No. Hei 1 / 1989 – 221304, etc.

As an antimicrobial soluble glass, for example, use can be made of, without any restriction, an antimicrobial soluble glass that contains a compound capable of eluting silver and / or copper ions disclosed in Japanese Laid Open Patent Gazette, Laid Open Patent Publication No. Sho 62 / 1987 – 158202, Japanese Laid Open Patent Gazette, Laid Open

Patent Publication No. Sho 62 / 1987 – 210098, Japanese Laid Open Patent Gazette, Laid Open Patent Publication No. Sho 63 / 1988 – 48366, Japanese Laid Open Patent Gazette, Laid Open Patent Publication No. Hei 1 / 1989 – 213410, etc.

As a silver salt compound, mention may be made of silver nitrate, silver chloride, silver sulfate, etc. as those preferable, however, it is to be understood that such a compound is not limited only to them. As a copper salt compound, mention may be made of a copper oxide, copper nitrate, copper chloride, copper sulfate, etc. as those preferable, however, it is to be understood that such a compound is not limited only to them.

Here there is no special restriction on ions that are co-present with silver ions and / or copper ions contained in these inorganic antimicrobial agents.

The polyurethane resin that coats the surface of the inorganic antimicrobial agent particles in accordance with the present invention can be obtained by allowing at least one kind of poly isocyanate compounds to react with at least one kind of compounds having 2 or more active

hydrogen – containing groups. In some cases, it is permissible to use water in place of a compound having 2 or more active hydrogen – containing groups although the reaction rate is low, and it is also possible to utilize the water contained in such an inorganic antimicrobial agent. In this case, as the water contained in such an inorganic antimicrobial agent can be removed, a more preferable result can be obtained. Here if required, in order to accelerate the reaction, it is permissible to add a Lewis base (such as a tertiary amine, and a phosphine), an organic metal compound of a Lewis acid (such as an aluminum compound and a tin compound), etc. as a catalyst.

As a poly isocyanate compound, mention may be made of tolylene di-isocyanate (TDI), diphenyl methane –4, 4'- di- isocyanate (MDI), poly methylene poly phenyl poly isocyanate, hexa - methylene di- isocyanate (HDI), etc. as typical ones, however, it is to be understood that they are not limited only to the above - mentioned compounds. In addition, a block type isocyanate obtained by masking these compounds with a blocking agent such as phenol, thereby stabilizing them and making them

non- reactive at room temperature is more preferable due to the ease of handling. In addition since a poly isocyanate compound of a 100 % solid portion is in general high in viscosity and thus it is difficult to use it as is, it is preferable to dilute it with an appropriate solvent (such as MEK, xylene and ethyl acetate) for use.

As a compound having 2 or more active hydrogen – containing groups, mention may be made of a poly ester, a so- called poly ether polyol such as a poly (oxy propylene ether) polyol, and a poly (oxy ethylene propylene ether) polyol, an acryl polyol, a castor oil derivative and a tall oil derivative as typical ones, however, it is to be understood that they are not limited only to the above - mentioned ones.

The process for the production in accordance with the present invention characterized by coating the surface of particles of an inorganic antimicrobial agent with a polyurethane resin is characterized in that at least one kind of an inorganic antimicrobial agent particles, at least one kind of poly isocyanate compounds and at least of one kind of compounds having 2 or more active hydrogen – containing groups are

mixed while adding a catalyst if necessary. Here in a case of particles of an inorganic antimicrobial agent that contain water, even if a compound having 2 or more active hydrogen – containing groups is not added, the water therein undergoes a reaction, and thus it is possible to coat the surface thereof with a polyurethane resin.

In addition, in a case of a block type isocyanate compound, the block agent may be dissociated by the heat generated by the mixing or by heating if necessary, the active isocyanate groups are regenerated, and thus it becomes possible to allow them to react with a compound having 2 or more active hydrogen – containing groups or / and water.

In addition, the preferable total added weight ratio a poly isocyanate compound and a compound having 2 or more active hydrogen – containing groups with respect to the inorganic antimicrobial agent particles is in a range of 0.1 to 5 % by wt at which the antimicrobial performance may be displayed, though this naturally varies depending on particle sizes of an antimicrobial agent particles.

In addition, with the process for the production of the inorganic

antimicrobial agent in accordance with the present invention, mixing is in general carried out in air under atmospheric pressure, however it is permissible to carry out mixing under a different pressure or in an inert gas.

The configuration of the inorganic antimicrobial agent coated with a polyurethane resin in accordance with the present invention can be granular, powder or crushed, and selection may be made depending on use.

As for a resin to be used in the present invention, use may be made of a thermoplastic resin, a thermo- setting resin, cross linkage rubber, a synthetic fiber, a semi- synthetic fiber, and a regeneratd fiber singly or in combination. In addition, it is permissible for them to contain additives useful when added to these resins, such as a filler, a plasticizer, a stabilizer, a lubricant, an antioxidant, an ultraviolet ray absorbing agent, an electric charge preventing agent, and a pigment.

In terms of forms, the antimicrobial resin compositions in accordance with the present invention can be applied to a molded product (such as a

film, a sheet, a pipe and a formed product), a foamed product, a paint, an adhesive, a resin coating, fibers, and a composite material, however, there is not any special restriction on the forms, configurations, and sizes thereof. In a case of fibers, it is possible to use it as a woven product, paper, a non – woven cloth, etc. by combining it with a fiber of a different type, which is not an antimicrobial resin composition. In addition, as to the ratio of the above - mentioned inorganic antimicrobial agent particles with respect to the total weight of the composition, if it is less than 0.05 % by wt, the antimicrobial effect can not be displayed, while if it exceeds 30 % by wt, the characteristics of a resin are markedly damaged and it can not be used. More preferably, a range of 0.1 to 5 % by wt is to be selected.

With the process for the production of the antimicrobial resin composition in accordance with the present invention, an inorganic antimicrobial agent coated with a polyurethane resin is, for example, mixed with a resin and molded by means of an injection molding machine. It is also permissible to prepare a master batch with a resin or a

wax of the same quality as the resin to be used in the final use, and then to dilute it with a virgin resin so as to achieve a pre- determined antimicrobial agent concentration.

[Effects of the Invention]

As the inorganic antimicrobial agent coated with a polyurethane resin in accordance with the present invention does not have a hygroscopic property, it is easy to handle it. And it can be dispersed well in a resin, it is rich in heat resistance, it does not discolor a resin at all, and it displays an excellent antimicrobial property. An antimicrobial resin composition obtained by adding this to a resin can be used to provide wide ranging products having an antimicrobial and antifungus properties such as sundry resin goods, packaging products for food, clothing, leather for automobile interiors, etc.

Examples Embodying the Invention

In the following we shall explain the present invention in detail by referring to some examples embodying the invention. Here we explain

antimicrobial zeolite, as an example, which is a typical inorganic antimicrobial agent.

Example 1 for Reference (Preparation method of antimicrobial zeolite)

Silver nitrate in an amount of 8.5 g was dissolved in 500 ml of distilled water, and while stirring it, 8.1 ml of 28 % aqueous ammonia was added thereto. Then, the initial brown turbidity became transparent, and an aqueous solution of a silver ammine complex was produced. The pH value at this time was 10.7. While stirring this solution, 250 g of a dried product A type zeolite (average particle diameter : 3.5 μ m, and specific surface area : 750 m^2 / g) of a sodium type was added thereto, and they were allowed to undergo a reaction at room temperature for 3 hrs. After the reaction, the reaction product was filtered, washed with distilled water, and dried at a temperature of 100 $^{\circ}$ C, and thus white antimicrobial zeolite was obtained (Sample 1). The quantity of the silver ammine complex carried on this antimicrobial zeolite was 2.0 % by wt when converted into silver ions.

Example 1 (Preparation of an inorganic antimicrobial agent coated with

polyurethane resin)

The antimicrobial zeolite prepared in Example 1 for Reference (Sample 1) was left undisturbed overnight indoor, and allowed to sufficiently absorb humidity. One hundred g of this antimicrobial zeolite was placed in a high speed mixer (made by Naniwa Chemical). Then a mixture prepared by mixing 0.94 g of block type isocyanate of a hexa- methylene di- isocyanate (HDI) series (made by Nippon Polyurethane Kogyo, Coronate 2507; solid portion, 80 % by wt: MEK, 20 % by wt: and effective NCO, 11.6 % by wt) and 0.6 g of polyol (made by Nippon Polyurethane Kogyo, Nippolane, 1100: solid portion, 100 % wt; and hydroxyl group value, 205 to 221) in advance was poured into the mixer, followed by stirring at a rate of about 5000 revolutions per min. The temperature in the mixer was increased by the frictional heat due to mixing, and the agitation continued further for 20 min after the temperature had reached 150 °C. Thereafter, the agitation was stopped, and it was cooled down naturally. As the product thus obtained was granular, it was lightly crushed by use of a crucible, and powder of an

inorganic antimicrobial agent coated with a polyurethane resin of 1.5 % by wt according to calculation was obtained (Sample 2). Similarly, powder of an inorganic antimicrobial agent coated with a polyurethane resin of 3 % by wt according to calculation was obtained (Sample 3).

Example 2 (Humidity absorption test of an inorganic antimicrobial agent coated with a polyurethane resin)

Powder of an inorganic antimicrobial agents coated with the polyurethane resin prepared in Example 1 (Sample 2 and Sample 3) was left undisturbed indoor overnight, and a humidity absorption test was carried out. The results are given in Table 1. From the results, it was understood that the powder of the inorganic antimicrobial agents coated with a polyurethane resin had hardly any humidity absorption property.

Table 1

Sample	Initial water content	Water content after leaving undisturbed overnight
Sample 2	4.1 %	4.1 %
Sample 3	3.8 %	3.8 %

Example 3 (Silver ion elution concentration of the inorganic antimicrobial agent coated with the polyurethane resin)

The powder of the inorganic antimicrobial agents coated with the polyurethane resin prepared in Example 2 (Sample 2 and Sample 3) was placed in a quantity of 0.1 g respectively) in a beaker that contained 50 ml of pure water, and after stirring it for 30 min by a stirrer, it was filtered. The silver ion elution concentration of the filtrate was measured by means of an ion meter (made by Denki Kagaku Keiki, IOL – 30) (Table 2). From this result, one can sufficiently expect an antimicrobial effect.

Table 2

Sample	Silver ion elution concentration (μ g / l)
Sample 2	26.5
Sample 3	17.6

Example 4 (Preparation of an antimicrobial resin composition)

The powder of the inorganic antimicrobial agents coated with the

polyurethane resin prepared in Example 1 (Sample 2 and Sample 3) was kneaded into a poly propylene resin (Tonen Kagaku, J – 409) by use of an extrusion molding machine (set temperature, 220 °C) so that 1 % by wt might be achieved, and test pieces of 30 x 40 x 2 mm (respectively to be referred to as Sample 5 and Sample 6) were obtained. These test pieces were compared with other blank test pieces prepared without adding the inorganic antimicrobial agent (to be referred to as Sample 4), and it was found that they were very good to the extent that they could not be distinguished at all.

Example 5 (Antimicrobial tests of the antimicrobial resin compositions)

Antimicrobial tests were carried out by use of E ccoli (IFO 3301) and staphylococci (IFO 3060) by the pressured close contact method.

The test pieces obtained in Example 4 (Sample 4, Sample 5 and Sample 6) were placed in bags made of polyethylene film (Mitsubishi Yuka, LS – 30, film thickness, 30 μ m) which could accommodate the test pieces of 30 x 40 x 2 mm. After introducing 0.1 ml of one of the microbial liquids separately cultured in one of the bags in a dropwise manner, the air in the

film was exhausted, and then it was sealed. Thereafter, it was pressured by a weight, and placed in an incubator, and after 24 hrs, the remaining live microorganisms in the bag was washed out with a phosphoric acid buffer solution (3 ml). For 1 ml of this wash liquor, the number of live microorganisms was measured by use of an SCDL agar – agar culture medium by the mix – dilution flat plate culture method. The results thus obtained are given in Table 3. From these results, it can be seen that they showed good antimicrobial effects.

Table 3

Sample	E. coli	Staphylococci
(No. of microorganisms initially added)	5.5×10^4	4.2×10^4
Sample 4 (blank)	7.3×10^5	1.3×10^5
Sample 5	< 10	< 10
Sample 6	< 10	4.4×10^1

Applicant for Patent Shintokogio Ltd. (seal impression)

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